二氧化碳地质储存中的反应溶质运移数值模拟

Reactive Transport Modeling for CO_2 Geological Sequestration

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Issues Can be Addressed by Reactive Transport Modeling反应溶质运移模拟可以解决的问题

- Changes in groundwater quality induced by CO_2 injection (storage formation and shallow aquifers)

  由CO_2注入引起的地下水水质变化（储层和浅部含水层）

- What is the long-term fate of injected CO_2?

  注入的CO2最终归宿?

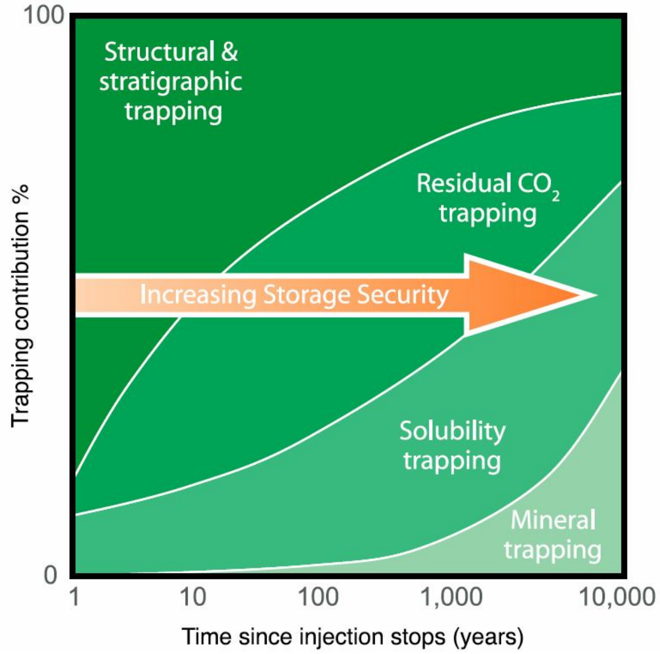
- What fraction of CO_2 is stored as a free phase (mobile or trapped), dissolved in the aqueous phase, or sequestered in solid minerals?

  注入的CO2以不同形式被封存的比例?

- How do the proportions in these different storage modes change over time?

  不同储层形式随时间的变化?

- Is co-injection with H_2S feasible?与H2S共同注入是否可行?
- Caprock integary?盖层整体安全性?



(After IPCC)

Simulator TOUGHREACT模拟器

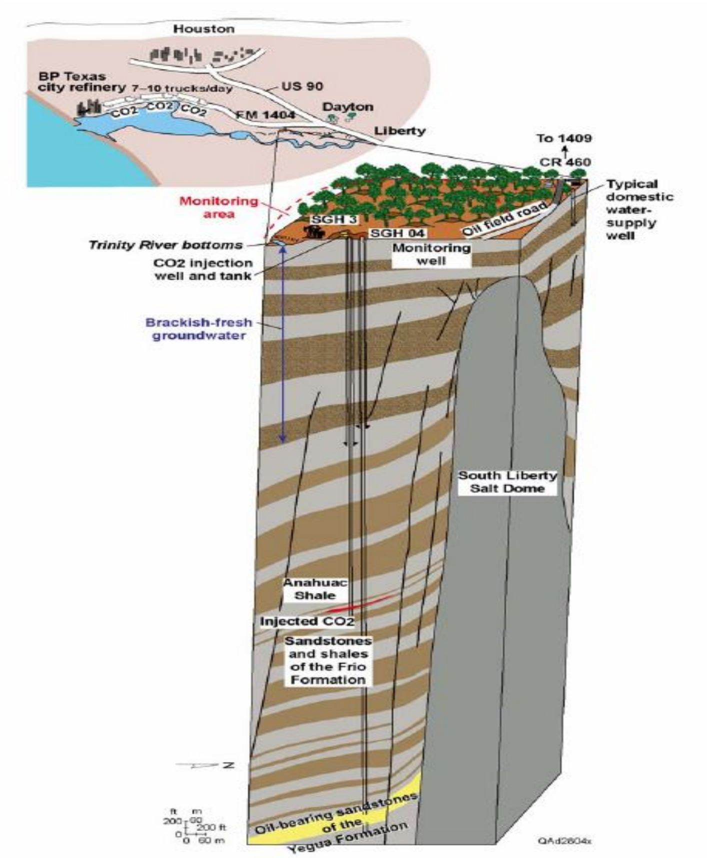
Processes（过程）:

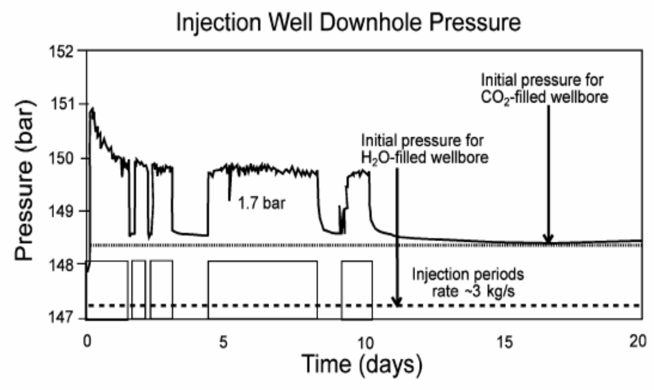
- Multiphase fluid and heat flow: TOUGH2 V2 (Pruess, et al., 1999)（流体和热模拟）
- Transport: advection and diffusion in both liquid and gas phases（溶质运移模拟）
- Chemical reactions: （化学反应模拟）
  - Aqueous complexation 水相络合物
  - Acid-base 酸性机制
  - Redox 氧化还原机制
  - Mineral dissol./precip. (equilibrium and/or kinetics)
    矿物质溶解沉淀（平衡或动态）
  - Gas dissol./exsol. 气体溶解析出
  - Cation exchange 阳离子交换
  - Surface complexation 表面络合
  - Linear Kd adsorption 线性Kd吸附
  - Decay 衰减

Special Features 特点:

- **Changes in porosity and permeability, and unsaturated zone properties due to mineral diss./ppt. and clay swelling**
  由于矿物质溶解/沉淀和粘土膨胀引起的孔隙度和渗透率以及非饱属性的变化
- **Gas phase and gaseous species are active in flow, transport, and reaction**
  气相和水相物质在流动、运移和化学反应中是活跃的
- **General: Porous and fractured media; 5 ϕ-k models; rate laws; any number of chemical species**
  常规的：孔隙和裂隙介质，**5 ϕ-k** 模型；速率定律；任何数量的化学物种
- **Wide range of conditions: P, T, pH, Eh, Salinity**
  宽泛的应用条件：压强，温度， **pH,** 电势以及盐度
- **Widely used: institutions, J. Papers**
  广阔的应用领域：许多研究机构以，发表了许多论文

Water Chemistry in the Observation Well Induced by CO2 Injection at Frio

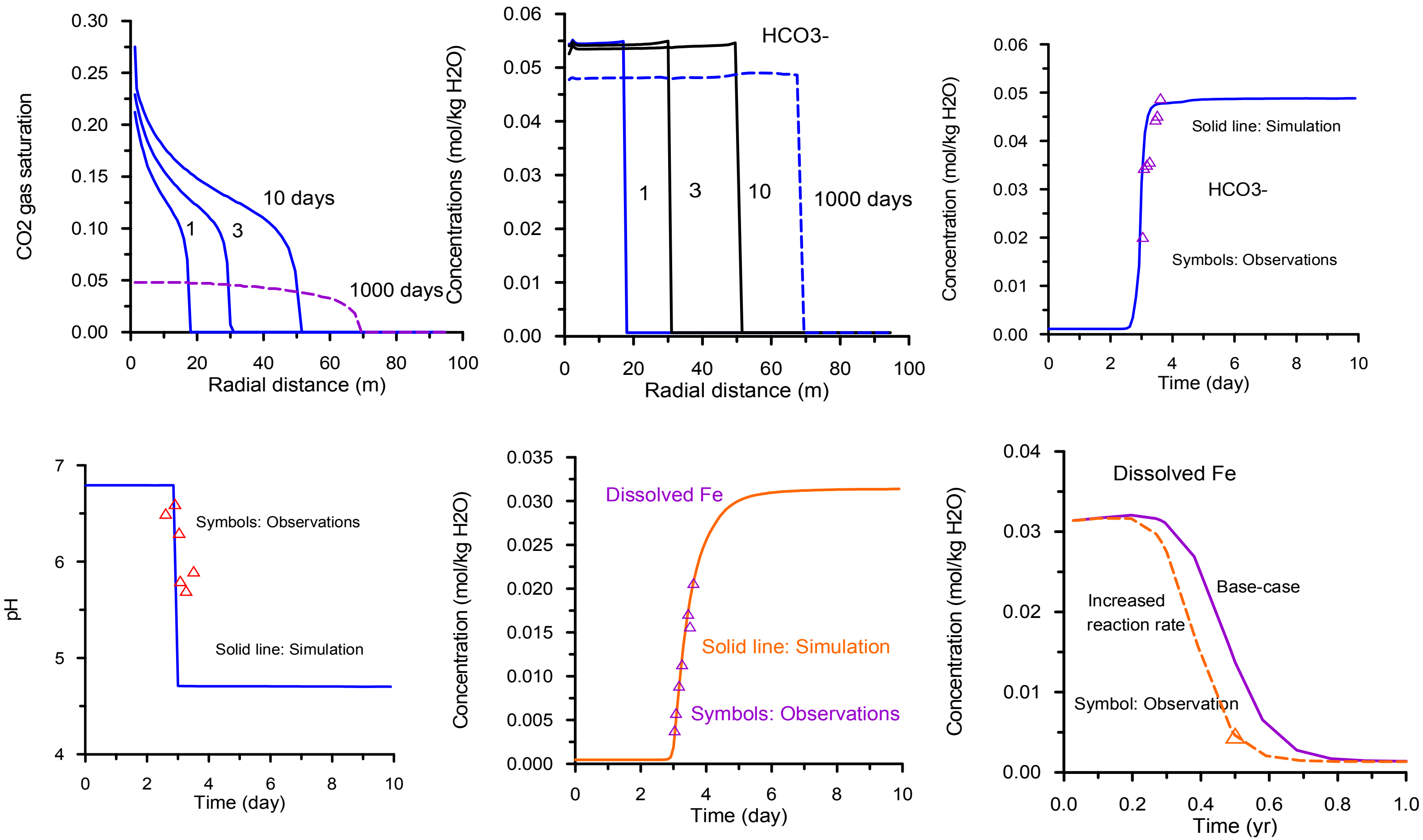




Mineral	Chemical composition	Vol.% of medium Sand	Vol.% of medium Shale
***Primary*:**			
quartz		40.6	17.3
kaolinite		1.41	3.95
calcite	$CaCO_3$	1.35	9.81
illite		0.7	25.33
kerogen-OS		0.0	1.8
oligoclase		13.86	4.75
K-feldspar		5.74	4.27
Na-smectite		2.8	20.7
chlorite		3.19	2.12
hematite		0.35	0.0
porosity		30	10
***Secondary*:**			
anhydrite	$CaSO_4$		
magnesite	$MgCO_3$		
low-albite			
dolomite	$CaMg(CO_3)_2$		
siderite	$FeCO_3$		
Ca-smectite			
pyrite			
ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$		
dawsonite	$NaAlCO_3(OH)_2$		
alunite	$KAl_3(OH)_6(SO_4)_2$		

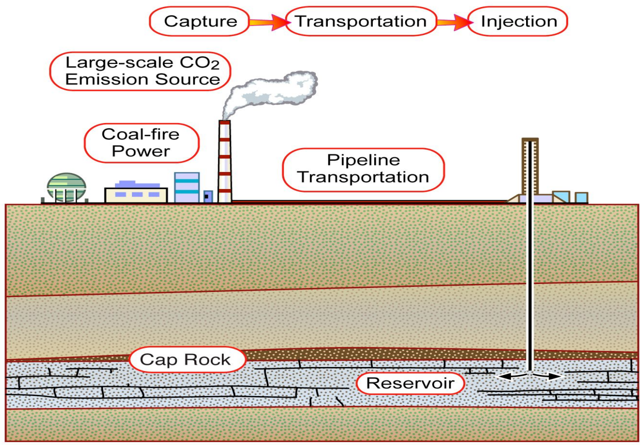
Component	*Concentration (mol/kg H_2O)*
Ca^{2+}	6.6×10^{-2}
Mg^{2+}	2.2×10^{-2}
Na^{+}	1.35
K^{+}	4.53×10^{-3}
Iron	4.63×10^{-4}
SiO_2(aq)	2.50×10^{-4}
Carbon	5.04×10^{-2}
Sulfur	4.20×10^{-5}
Al^{3+}	1.56×10^{-8}
Cl^{-}	1.49
O_2(aq)	4.88×10^{-68}
pH	6.7
T	59°C

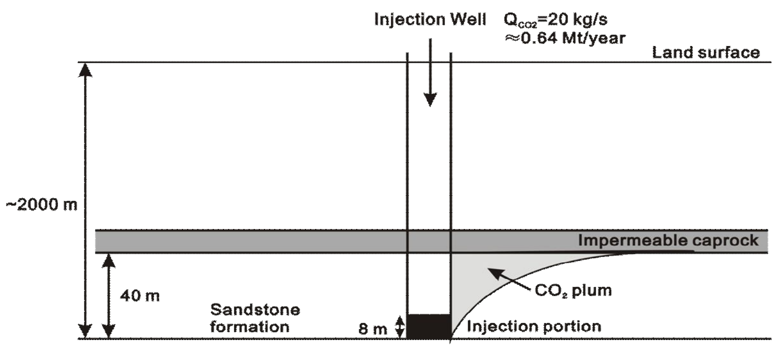
Water Chemistry Change: Results



Chemical Geology; Xu, Kharaka, Doughty, Freifeld, and Daley; 2010

Long-term Storage of CO_2 CO_2的长期储存





Schematic representation of the 2-D radial flow model for supercritical CO_2 injection into a sandstone formation.

- **2-D radial model for long-term CO_2 storage. Use physical and chemical conditions and parameters as in the previous 1-D radial example**

  CO2的长期储存二维径向模型

- **Consider density changes due to reactions (aqueous complexation of bicarbonate with dissolved cations) such as $NaHCO_3$, $CaHCO_3^+$, $MgHCO_3^+$, and $FeHCO_3^+$, …**

  考虑由于反应引起的密度变化

Gas and Aqueous Phases

气相和水相

- CO_2 injected into a storage reservoir will tend to migrate upwards towards the cap-rock because the density of the supercritical CO_2 phase is lower than that of the aqueous phase

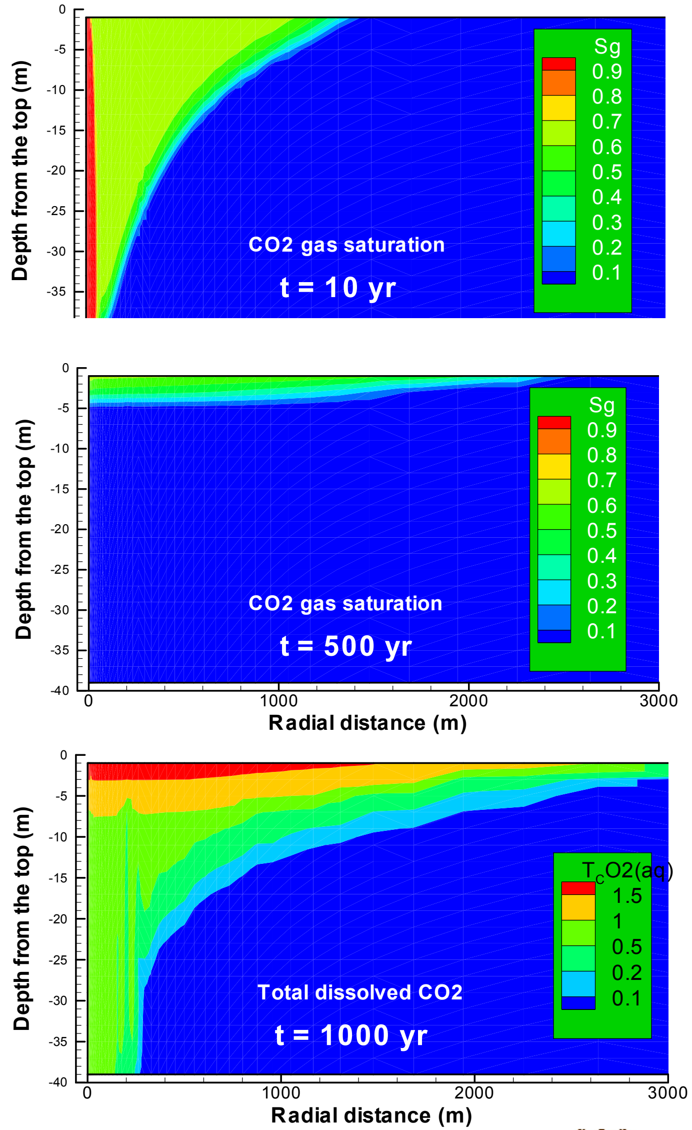
  储层中注入CO2趋向向上面的盖层运移，因为超临界的CO2密度低于水的密度

- In the upper portions of the reservoir, CO_2 dissolution into brine lowers pH and induces mineral dissolution

  在储层的上部，CO2溶解于盐水中使pH降低，并导致矿物溶解

- Then aqueous complexation of bicarbonate with dissolved cations: $NaHCO_3$, $CaHCO_3^+$, $MgHCO_3^+$, and $FeHCO_3^+$, increase density, and enhance convection mixing

  水中碳酸氢根的络合物以NaHCO3,CaHCO3+, MgHCO3+和FeHCO3+溶解离子存在，增加水的密度，加强对流混合作用



Porosity Change and Mineral Trapping

孔隙变化与矿物捕获

- **Lowed pH induces dissolution of primary minerals and precipitation of clay and carbonate minerals**

  低pH导致主要矿物的溶解和粘土矿物和方解石矿物沉淀

- **Porosity increases slightly in the two-phase region due to dominant mineral dissolution. While porosity decreases at the front of the aqueous-phase**

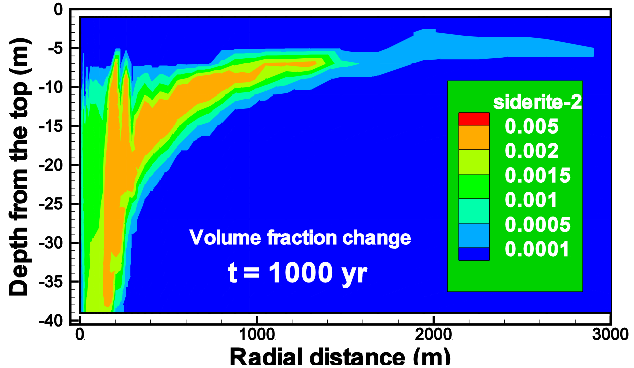
  由于矿物溶解为主，导致两相混合区孔隙度的稍微增加，水相前沿的孔隙 度减小

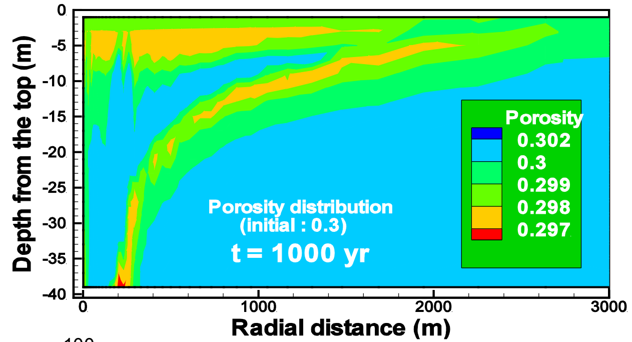
- **The mineral trapping starts at late stage and then increases with time**

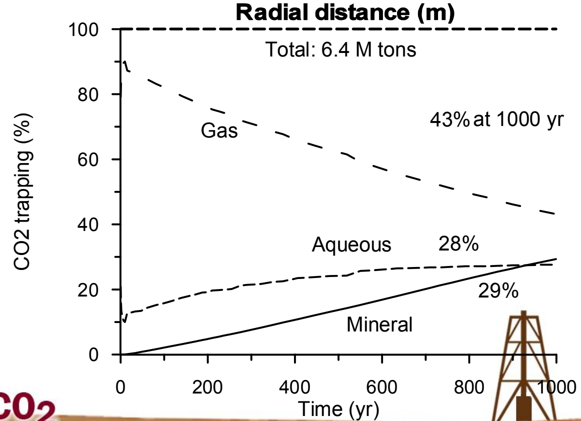
  后期矿物捕获开始并随着时间增长

- **After 1,000 years, 29% of the injected CO_2 can be trapped in the solid (mineral) phase, 28% in the aqueous, and 43% in the gas phase.**

  在1000年后，29%的注入被固体矿物捕获，28%的溶解于水中，43%的以气体（超临界）存在



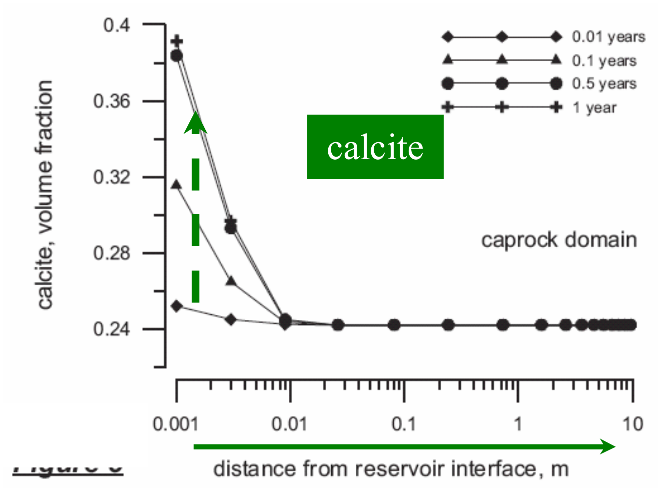


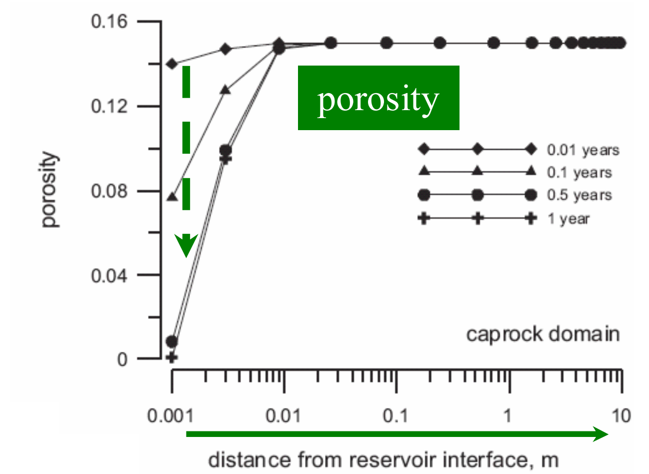


Cap Rock Alteration due to CO_2 Storage

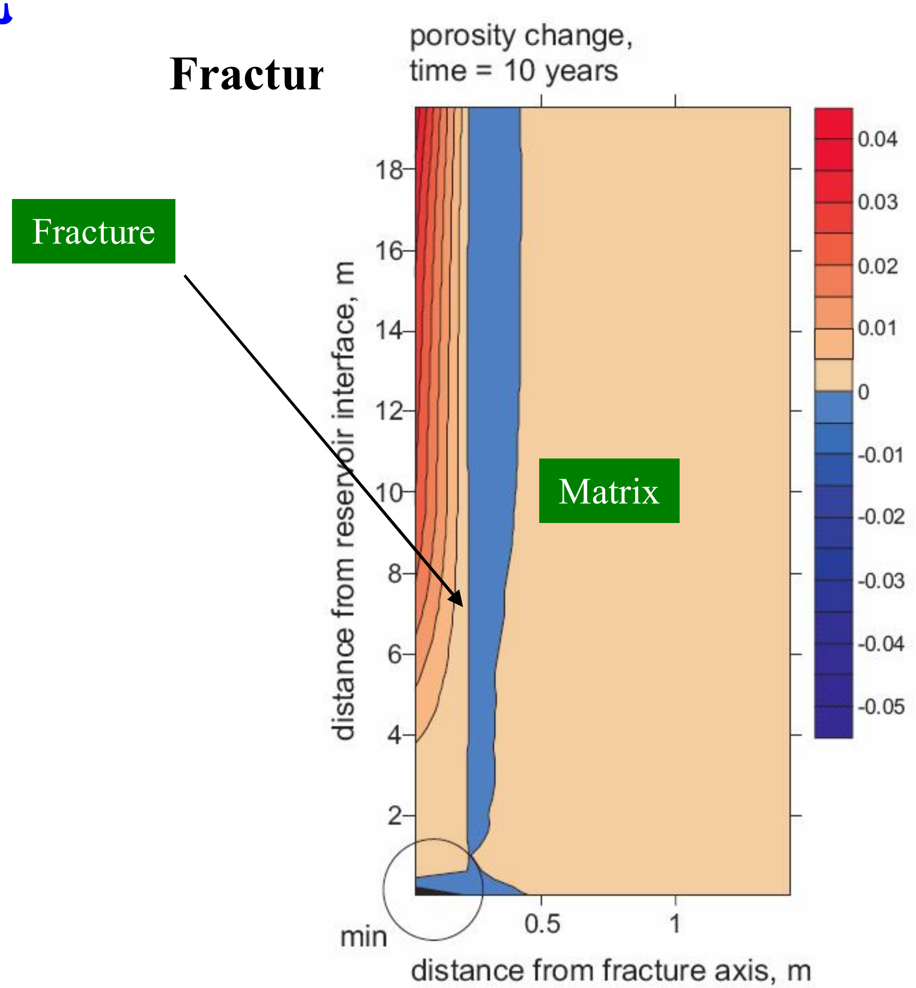
CO_2储存引起的盖层变化

Self sealing



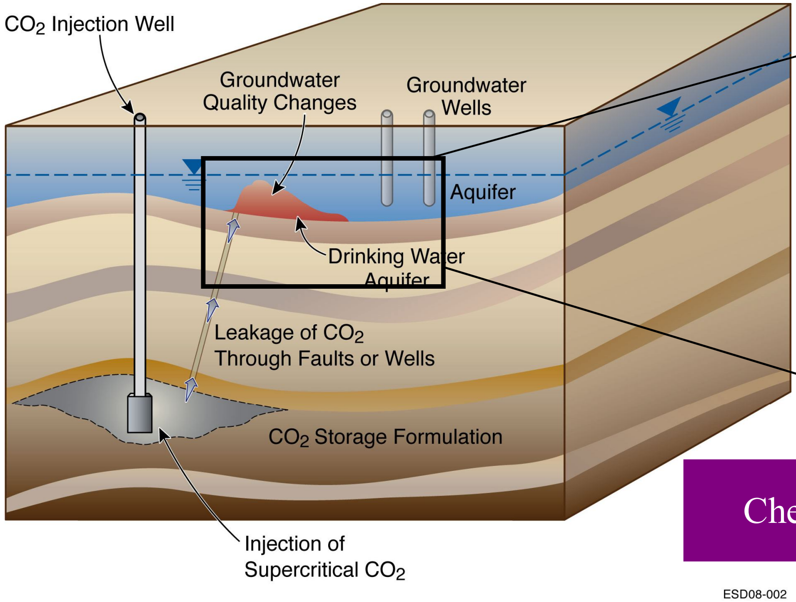


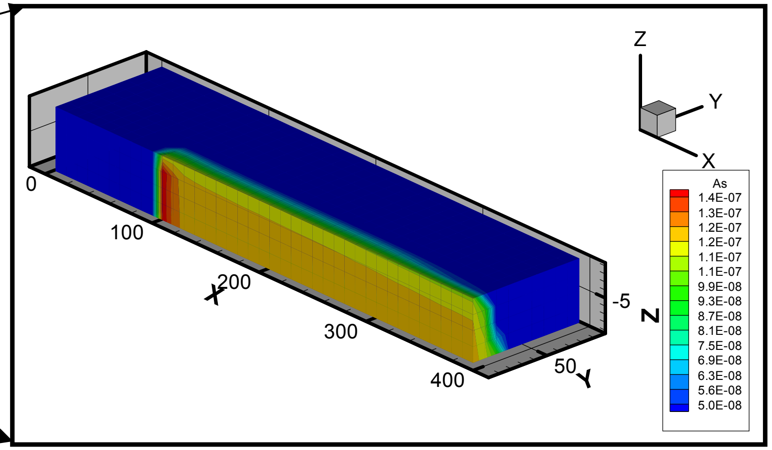
Fractur



(F. Gherardi, T. Xu and K. Pruess, Chem. Geol., 2007)

Change of groundwater quality: heavy metal
地下水质变化：重金属

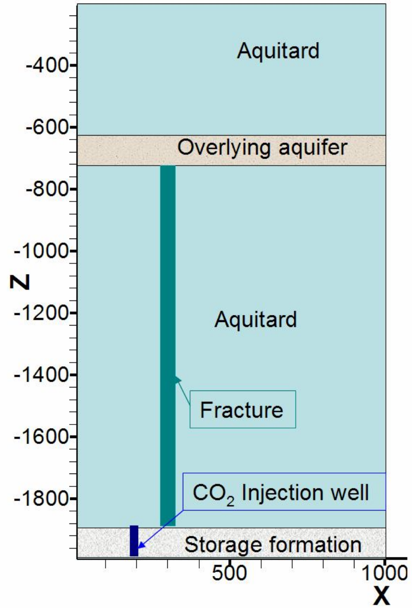




Chemical Geology; Zheng, Apps, Zhang, Xu, and Birkholzer; 2009

- **Possibility of leakage pathways such as faults or wells**
  可能的泄露路径：断层或井
- **CO2 leakage into aquifers may cause mobilization of hazardous trace elements**
  泄露到含水层可能导致有毒痕量元素的迁移
- **Reactive transport modeling shows that substantial increases in aqueous concentrations of lead and arsenic could occur**
  反应溶质运移模拟显示水相中主要成分如铅和砷的浓度的不断增加

Change of groundwater quality: organics
地下水质变化：有机物

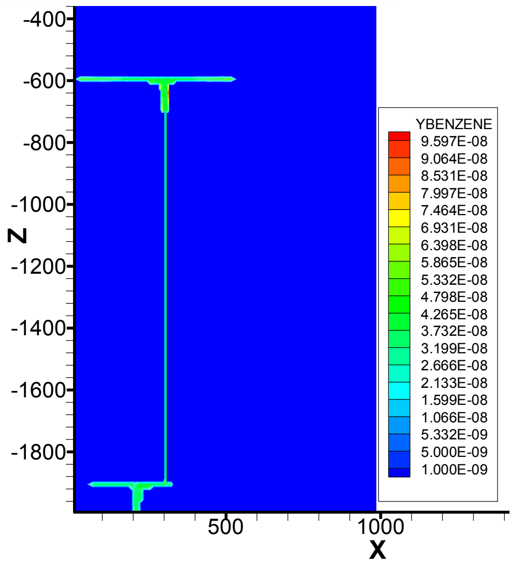


Leakage of CO2 or brine migration may cause migration of other contaminants (e.g., organics, co-injectants) into aquifers

CO2泄露或是盐水迁移可能导致其它污染物迁移到含水层

Model study indicates that benzene could be extracted by supercritical CO2 from storage formation and transported to an overlying aquifer via fracture

模型研究表明苯可能被超临界CO2从地层中析出并通过裂隙运移到上部的含水层



Research Ongoing; Zheng, Apps, Spycher, Xu, and Birkholzer

Model Validations
模型识别校正

- **Can be partially validated from:**
  能够通过以下方式部分校正：
  - **Lab experiments: Batch and flow-through**
    实验室实验：静态实验和流动驱替
  - **Observations from field demonstration projects**
    场地工程观测
  - **Analogue from CO_2 reservoirs**
    CO_2储层类比
- **Here the validation concept is different from conventional groundwater modeling:**
  此处识别的概念与传统地下水模拟不同：
  - **Pattern, mineral assemblage**
    矿物存在形式和组合
  - **Qualitative, semi-quantitative**
    定性的，半定量

Natural Analogue
天然CO2气田比拟法

- **Mineral alteration in Ladbroke Grove CO_2 (gas) field of South Australia.**

  矿物变化

- **Observations consistent with our simulations include the destruction of chlorite and net corrosion of the feldspars, a reduction in the concentration of calcite, an increase in the concentration of siderite and ankerite.**

  观测矿物变化和计算值一致，包括绿泥石破坏和长石的网状溶蚀，碳酸钙浓度的减小，菱铁矿和铁白云石浓度的增加

1460 *M.N. Watson et al. / Energy 29 (2004) 1457–1466*

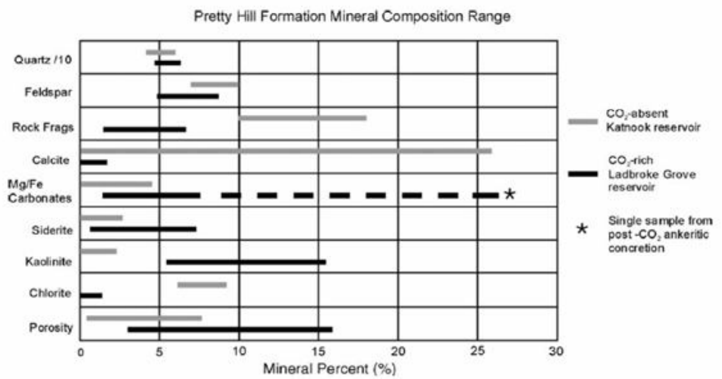


Fig. 2. Comparison of mineral compositions from the CO_2-rich Ladbroke Grove and the CO_2-absent Katnook samples. Variation in mineral composition is very apparent in carbonates and clays.

Open Challenges (Uncertainties)
面临的挑战(不确定性)

- Processes are multi-scale in space and time
  过程在空间和时间上是多尺度的
  - The time scale for significant convective mixing is likely to be slow, on the order of hundreds of years or more
    时间尺度上，对流混合重要过程可能非常慢，大约在百年的数量级上或是更多
  - Kinetics of geochemical interactions
    化学反应动力学
- Depend on many factors including initial abundance of primary minerals, and pressure and temperature conditions of storage formation
  取决于多因素包括主要矿物的初始浓度，储层压力和温度条件
- Thermodynamic data especially for highly-concentrated solutions: Lab experiments and analogues of natural CO_2 reservoirs
  热动力学数据,特别是高浓度的溶液，室内实验和天然CO2储层类比
- Reactivity of SC CO_2 with rock and organic matters is not well understood
  SC CO2和岩石及有机质的反应过程还未清楚
- Significant changes in porosity could occur, a mechanics model needs to be coupled with a reactive transport model
  孔隙度可能会发生重大变化，需要反应该机理的模型和反应溶质运移模型进行耦合
- …

Conclusions (1)
结论（1）

- Reactive transport modeling can solve problems and answer questions related to CO_2 geological sequestration, such as
  反应溶质运移模拟能够解决和回答与CO2地质封存相关的问题，例如：
  - fate and transport of injected CO2 注入的CO2归宿和运移
  - amount of CO2 dissolved in groundwater 地下水中溶解CO2的数量
  - trapped by carbonate minerals 碳酸盐矿物捕获
  - variations of these storage forms over time. 储存形式随时间的变化
- Comprehensive geochemical transport models such as TOUGHREACT have been developed that incorporate
  综合的地球化学运移模型（例如TOUGHREACT ）已经开发出来了，主要包括
  - aqueous reactions 水相中的反应
  - mineral dissolution and precipitation under equilibrium and kinetic conditions 平衡或是动力条件下的矿物溶解和沉淀
  - CO2 dissolution and exsolution CO2溶解和析出
  - coupled to multi-phase CO2-water flow 耦合CO2-水多相流

Conclusions (2)

- **These models have been applied to solve field-scale problems at various sites such as**

  这些模型应用到各个场地中解决区域尺度的C02储存问题
  - **Sleipner in the North Sea,**
  - **Alberta basin of Canada,**
  - **the U.S. gulf coast**
  - Australia,
  - China,..
- **Reactive transport modeling is also an important tool to study storage security, caprock integrity, and degradation of wellbore cements.**

  反应溶质运移模拟被用作研究储层安全性、盖层整体性和井孔水泥腐蚀的重要工具
- **Leakage from CO2 storage formations into potable aquifers and its impact on groundwater quality is a potential concern, which can be best studied through reactive transport modeling.**

  通过反应溶质运移模拟，可以评价CO2从泄露到可饮用的含水层中地下水水质的潜在影响
- **The model can be only partially validated by Lab, Field, Natural.**

  模型能够通过实验室、野外和天然类比数据进行部分识别校正
- **Many open challenges (uncertainties) remain.**

  很多挑战（不确定性）仍然存在